

CEMENT AND LIME MANUFACTURE

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Properties of Portland Cement and Methods of Determining Them.

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DURING the past ten years our knowledge of Portland cement has been extended, due to the improved and new methods of examination, as well as to the considerably increased number of investigators. Cement users also have suggested improvements in the product, and have even at times showed their dissatisfaction with official specifications and standard methods of testing. Sometimes these suggestions could not be accomplished, but they have been of value in promoting intensive research work.

Portland cement research workers face many difficulties. The requirements regarding the properties of cement are created by the need of constructional practice, and the fact that cement is used in a mixture with other ingredients affecting the ultimate results makes the problem still more complicated. A satisfactory hardening process and sufficient strength are not the only properties required. Other phenomena of concrete or mortar, such as thermal effects, shrinkage and expansion, elasticity and creep, are also important; in spite of the immense amount of experimental work undertaken there is still no theory which accounts for all these phenomena, nor do we possess a clear conception of the properties of concrete.

The present methods of determining the mechanical resistance of concrete by tensile and compressive tests are by no means perfect. From the point of view of the producers they may be sufficient, giving comparative results of importance in the control of the production, but the results obtained by standard testing methods are not always related to those obtained in practice. The results for tensile or compressive strengths at the ages of 3, 7, or 28 days do not give an absolute guarantee of the strengths that will be obtained at later dates. More-

over, the most satisfactory test results up to 28 days are no security against a possible decrease of strength at later ages. The writer has encountered brands of cement which developed excellent strengths at early ages and complied with the usual tests for volume constancy, but did not produce a durable concrete. Attempts were made to explain similar facts by the insufficiency of our methods of testing for soundness. Different countries have adopted different methods for these tests, and generally they give reliable indications. Obviously, however, the existing methods do not satisfy all cement experts, since the United States cement manufacturers recently adopted a more exacting test for soundness¹. According to this method, 1 in. by 1 in. specimens either 5 in. or 10 in. long, made of neat cement, when cured in water in an autoclave at 420 deg. F. for three hours should not have an expansion of more than 1 per cent. Possibly this method may present a better criterion of volume constancy.

It is not surprising that the strengths established by the standard tests of cement mortar do not correspond with those obtained in concrete when it is considered that field tests made of the same concrete mix at different times often show large discrepancies. According to N. Davey², of the Building Research Station, "The engineer is often puzzled by the magnitude of the variations in strength of concrete test pieces made on a job. He may find that a set of test specimens made one day may be two or more times as strong as those made another day, yet, so far as has been practically possible, the cement, the quality of the aggregate, the water content, the proportions of mix, the method and time of mixing and the moulding of the test pieces have been kept the same throughout."

It is generally agreed that high tensile strength in a cement reduces the tendency toward cracking of concrete. The ability of concrete to resist tensile stress cannot with certainty be deduced from the standard tests for tensile strength, or from the compressive/tensile strength ratio, obtained by testing specimens of standard mortar gauged with 8 per cent. or 10 per cent. of water. Better comparative results have been achieved by testing 4 cm. by 4 cm. by 16 cm. prisms made of plastic mortar. Fair indications of extensibility have been obtained by testing a 6 in. by 32 in. concrete cylinder under sustained tensile load³.

Standard specifications usually prescribe the determination of fineness by means of sifting. Sieve tests do not show decisive results for the active fine part of cement. The same, in a smaller degree, can be said of the air elutriation test. Better comparative results are obtained by determining the specific surface by means of the Wagner turbidimeter⁴. The best indications of the granular composition of cement are obtained by means of sedimentation and the micro-measurement of the sizes of the separated fractions. Increased fineness improves the workability of concrete and increases the amount of water required for the normal consistency of cement paste; it, however, decreases the amount of mixing water required in concrete. Increasing the specific surface produces more gel during the process of hardening and consequently greater strength, especially at early ages; on the other hand, it causes a larger volume change and increases

the heat of hydration. By decreasing the amount of mixing water required to produce a workable concrete, finely-ground cement reduces the effect of "free water" in concrete; by favouring the formation of more gel, it diminishes the development of pores. These facts show the importance of a more effective method for determining the fineness of cement.

The heat generated by cement during setting and hardening has attracted attention during recent years. Two methods are used for its determination; namely, the solution method and the adiabatic method. Both give reliable results. Definite requirements regarding the heat of hydration are advanced chiefly in the United States, where the "heat-of-solution" method is used and the development of heat is expressed in calories per gramme of cement. This method consists in determining the heat of solution of unhydrated and hydrated neat cement in a mixture of nitric and hydrofluoric acids and the calculation of the heat of hydration by difference; a simple procedure for the test has been described by Wm. Lerch⁵. The amount of heat of hydration prescribed in various United States specifications for mass concrete (for the Morris and Boulder dams, for instance) as not exceeding 65 cal. per gramme of cement at 7 days and 80 cal. per gramme at 28 days, stimulated the manufacture of so-called "low heat" cements. In the writer's opinion the limitation of heat liberated during the hydration of cement to definite figures is of minor importance and may lead to false consequences. The special cements which generate less heat have lower strengths at early ages than normal cements. The writer would prefer to specify the heat of hydration not in definite figures, but in ratios of the strength produced by a unit of cement to its heat of hydration. In this case the seeming advantage of low-heat cement for mass construction may be considered in its true light, and disappointments caused by the slow and insufficient hardening of these brands, when placing concrete at lower temperature, avoided.

In practice it is important to use a cement possessing reasonably slow stiffening properties. The well-known mechanical methods for determining setting time, indicating the beginning of setting of cement paste, give the user a certain security regarding the time of mixing and placing mortar or concrete. For the same purpose two other methods, the thermal and electrical, are known. The first is not accurate. The second, based on measuring the conductivity of cement paste or mortar, gives more accurate results than the mechanical and thermal methods, but unfortunately it is not adopted by any of the official specifications and is very seldom used.

Until a few years ago it was generally agreed that the major constituents of cement are represented by the four compounds $3\text{CaO} \cdot \text{SiO}_2$, β - $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. The researches of the United States Bureau of Standards, particularly those of R. H. Bogue, advanced the method of computation of the principal compounds in cement from the oxide analysis. Inasmuch as the properties of these compounds were known, such a calculation should make it possible to determine the properties of cement from the values established by the chemical analysis. Later F. M. Lea and T. W. Parker proved

that Bogue's formula covers a special case, when the compounds crystallise to complete equilibrium. Lea introduced a formula based on an equilibrium frozen from clinkering temperature. According to Lea the two formulae express extreme conditions; in fact, he says, "The stage in which part of the liquid crystallises and part becomes glass seemed most obviously the real condition in clinker; moreover, different clinkers appeared to vary within this intermediate stage."⁶ The seemingly simple conditions became suddenly complicated. In 1936 a note communicated by the Director of the United States National Bureau of Standards stated, "It thus appears that poor correlations obtained between the physical and chemical properties of cements and their calculated compound compositions may be due to inaccuracies in the method of computing the compound composition."⁷

An opinion was expressed that the formula of Bogue should be modified, but the writer does not see any practical value in such a modification at present. Despite its inaccuracy Bogue's four-compounds method is the most simple one in obtaining valuable comparative results. Its application was very useful for the cement manufacturers. Strictly speaking, at present no formula based on the chemical composition of cement can predict its properties exactly, because two cements from different cement plants but of identical chemical composition in regard to the contents of oxides, differ largely in their properties as hydraulic hardening materials. The difficulties of chemical investigation of cement are well known, and are general in silicate chemistry. The silicates, as a rule, cannot be dissolved without being decomposed. The complex nature of the silica compounds and their high melting point, combined with high viscosity making reactions very slow, result in the fact that only in rare cases can constant equilibrium be reached. These difficulties in physico-chemical methods of research and in obtaining knowledge of the important phenomena of the crystallisation and hydration of cement, result in chemical investigation being, as W. Eitel⁸, Director of the German Institute for Silicate Research, has pointed out, "easily deformed by non-equilibrium."

The first scientifically-proved information of the nature of Portland cement is a result of the petrographic method of investigation. The studies of thin sections of clinker started several decades ago and established the four crystalline formations. After the fundamental work by von Glaserapp in 1912, this method did not produce any new ideas on the constituents of clinker. But, together with the synthetic method of the Geophysical Laboratory of the Carnegie Institution of Washington which created the foundation for a better understanding of the reactions between silica and metallic oxides in a state of fusion, it enlarged our conception of the nature of cement clinker. As a rule the cement manufacturer did not use the petrographic method for the control of production, but where the petrographic examinations were frequently made comparative results were achieved which were of great value in estimating the uniformity of burning. The method of thin sections has, however, the disadvantage that it is impossible to grind sections thinner than 20 microns. This disadvantage is easily understood when it is considered that it is possible to observe a single crystal in section only

if the size of the crystal is greater than the thickness of the section. Inasmuch as the thin sections are 0.02 mm. and often 0.03 mm. thick, crystals of this size or smaller cannot be observed free from "overlap." This difficulty of micro-examination was recently partly removed by a new method worked out by Dr. Eng. B. Tavasci⁹, whose method, based on examining with reflected light the polished surface of a clinker etched with a suitable reagent, makes micro-examination independent of the thickness of the section. It was reported a few months ago¹⁰ that a different etching effect on individual constituents of clinker, depending on the kind of etching agent, could be established. For instance, an etching agent composed of 100 c.cm. of isoamyl-alcohol and 1 c.cm. of nitric acid detects C_3S but does not reveal C_3A and C_4AF ; a solution of 10 parts of oxalic acid in 90 parts of alcohol (95 per cent.) shows up C_3A but not C_4AF , C_3S , and C_2S . This new metallographic method appears to be very promising when used for determining the components of clinker.

Another method, which is of great importance for this purpose, is the X-ray examination of cement. This method was first applied in cement research by E. A. Harrington¹¹ and developed by other investigators, including W. C. Hansen, L. T. Brownmiller, and R. H. Bogue. A powdered material subjected to X-radiation shows an X-ray diffraction pattern consisting of a series of lines in a definite position. Each crystalline individual has a characteristic diffraction pattern, which always appears to be the same, whether the compound is present in a pure state or intermixed with other compounds. If a compound enters into solid solution with another, the pattern will show the lines of the latter in a uniformly shifted position. The studies of Brownmiller and Bogue¹² seemed definitely to establish the compounds C_3S , C_2S , C_3A , and C_4AF as the chief constituents of clinkers. It was in accordance with the state of our knowledge when, about three years ago, it was stated in this journal: "The solid solution theory can be abandoned, and there is no longer any need to refer to Alite, Belite, Celite, and Felite, because the principal components of clinker can be expressed in proper chemical terms."¹³ The studies on the constitution of clinker made during recent years by the X-ray diffraction method show that the old conception of solid solution is not quite dead. It has been established that C_2S dissolves lime, that C_3S forms a solution with C_2S , and that Alite—the most important ingredient of cement—contains significant quantities of other compounds in solid solution¹⁴. The investigations on the system lime-alumina-iron oxide by the United States National Bureau of Standards¹⁵ indicate the presence of solid solution in this system. The studies on Celite by T. Yamauchi¹⁶ prove the formation of solid solution of limited miscibility and questions the existence of Brownmillerite in Celite-cements.

In these circumstances the application of a simple theory, considering cement clinker as a system of several separate compounds and a glassy co-substance, is, in the writer's opinion, not justified.

The micro-examination of the hydration of cement in conditions similar to those of constructional practice, i.e. in mixture with a small amount of water, is difficult. The examination of thin sections of set cement gives, due to the im-

perfect crystalline formation, an indistinct picture. A small amount of water results in very little crystallisation. E. Brandenberger, of the X-ray Laboratory of the Material Testing Institute of Switzerland, stated recently that there are indications that the X-ray diffraction method may be successfully applied for studying the hydration and setting of Portland cement¹⁷.

Purely chemical methods of investigation have not resulted in any essential development. The perchloric acid method introduced several years ago for determining silica gives correct analytical results and considerably shortens the time required by the old method. For the estimation of uncombined lime there are several methods; they all, from the glycerol method of W. E. Emley to the new ethylen-glycole method of P. Schaeffer and his co-workers, give reliable results. They are in some respects imperfect, because they estimate simultaneously the eventually existing "free lime" as well as lime-hydrate released from the calcium compounds of cement as a result of humidity during the storage or as a result of pre-hydration. For the qualitative micro-detection of uncombined lime in cement, natural oil of cloves has been recommended, and it is stated that this reagent is of advantage compared with that of A. White. While phenol reacts also with lime-hydrate, oil of cloves forms crystals with CaO only¹⁸.

Regarding the effect of the chemical composition on the qualities of Portland cement, it may be stated that, although its composition lies within certain limits, comparatively large fluctuations in the relationship of oxides are admissible. Strict general limitations to the content of some oxides cannot be justified by the present state of our knowledge. In a recent article¹⁹ the writer expressed an opinion on this subject; it is sufficient to say here that the most favourable composition should be established for each case depending on the nature of raw materials and the manufacturing conditions. The exact preparation of raw mix, as well as a sharp and uniform clinkering, are the sole rules which cannot be violated.

The writer has attempted to give a brief account of the methods of examination used at present, and their efficiency, in the estimation of the properties of Portland cement. The most important and generally used methods, are far from perfect, due to the complicated nature of cement as well as to the lack of a clear conception of concrete. The experimental work carried out during the last decade has greatly extended our knowledge, but this knowledge is of somewhat fragmentary character and it is still very difficult, if not impossible, to link it together into a coherent theory.

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Constituents of Portland Cement.

STUDIES on the minor constituents in commercial Portland cement clinker and in laboratory preparations of similar composition by microscopic and thermal methods are described by Messrs. H. Insley and H. T. McMurdie in Research Paper No. RP 1074 of the United States National Bureau of Standards. The microscopic methods included the examination of powdered preparations and thin sections with transmitted polarised light, polished etched sections with reflected light, and a combination of reflected and transmitted light using polished, etched thin sections.

The authors found that free MgO may be identified in polished unetched sections of commercial clinker and free CaO in sections etched with alcohol-water mixtures. Both free CaO and free MgO may be determined quantitatively in such sections.

The light interstitial material in cement clinker is shown to be $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. New determinations of the relations in the binary system $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ -MgO have been made. $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ takes less than 1 per cent. of MgO into solid solution.

The dark interstitial material consists of three types, namely, amorphous, rectangular, and prismatic. The amorphous material is glass. Characteristics and associations of the glassy material are given. Glassy material occurs in most commercial Portland cement clinker. The rectangular material is $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and is only rarely found in commercial clinker. The prismatic interstitial material frequently observed in commercial clinkers is probably a compound of lime, alumina and alkalis with a small amount of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ in solid solution. Its close similarity to $3\text{CaO} \cdot \text{SiO}_2$ in optical properties has prevented its identification by petrographic methods. It is readily distinguished from $3\text{CaO} \cdot \text{SiO}_2$ in polished sections by the use of suitable etchants. It is frequently found in commercial cement clinker with a moderately high $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio. Laboratory-prepared clinker composed of CaO, Al_2O_3 , Fe_2O_3 and SiO_2 when cooled at moderate rates, contains rectangular dark interstitial material, whereas the same preparation with small amounts of Na_2O , K_2O , or both, contains prismatic dark interstitial material. The K_2O compound forming the prismatic crystals has not been identified. The Na_2O compound has properties very like those of the compound to which the formula $8\text{CaO} \cdot \text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3$ has been assigned by its discoverer.

Changes in composition of the minor constituents depending upon chemical composition and cooling condition of the clinker are discussed, and difficulties in quantitative determination of the compound composition of clinker are enumerated.

Prevention of Accidents.

WORKS SAFETY PROPAGANDA.

The following is an abstract of an address given by Mr. B. L. Lelliott, Welfare Officer of the Associated Portland Cement Manufacturers, Ltd., at the recent conference of the National Safety-First Association.

An analysis of machinery accidents will no doubt reveal that the vast majority are due, not to inadequate guarding, but to human failing on the part of the victim or of some other person. Machine guarding, however good, does not ensure freedom from machinery accidents. As much care and attention must be given to the education of those working on or near the machines as to fencing and guarding. Over 75 per cent. of the industrial accidents in this country have nothing to do with machinery; human failings are responsible for most of them. Discipline inculcated by rules may make some contribution to their reduction, but for accidents due to thoughtlessness, carelessness, dangerous practices, and the like, carefully planned schemes which solicit and maintain the interest of every person on the factory are essential. Propaganda is a necessary and important part of any effective safety campaign.

Safety organisers should provide executives with information on safety, including: (1) Monthly reports on facts revealed by the works accident register; (2) comprehensive annual report giving yearly comparisons of accident figures; (3) minutes of any safety committee meetings, or findings of committees investigating accidents; (4) information on safety devices particularly suitable for the industry; (5) extracts from publications dealing with the subject.

No one kind of propaganda will appeal to every man; it ceases to have any influence after a time, however excellent, if it is kept up too long. Novel ideas and original ways of presenting them are of the utmost importance.

Perhaps the most common medium for propaganda is the poster. Although quality of design may be important, in this country many excellent posters are wasted through poor methods of display. Poster boards can be the "shop window" of the safety organisation. Therefore care should be taken that they are attractive, and placed in the best positions where they are likely to be noticed. Boards need not necessarily be reserved always for posters. In fact, it is sometimes wise to leave them blank for a few days and then use them for the display of smaller safety devices, such as goggles, eye shields, gloves, etc., or a collection of things which might have led to accidents. The production of "home-made" posters can be encouraged by offering small prizes. The practice of using portable boards is also a good one. If the position of the boards is continually changed the men do not know where they are going to find a poster next. Another good plan is occasionally to fix a poster board to the side of a loco or other vehicle which runs about the works.

Of the many means devised to interest employees in accidents none is better than a competition. The competing units can be works, departments, sections of departments, or teams chosen arbitrarily. Many men who apparently give no thought to their own safety will co-operate if they know that an injury due to

their own thoughtlessness or carelessness may discredit their department or let down their team. The rules of the competition should be simple and should state which accidents shall count and what shall constitute the basis of the competition in order to determine the winner. Some of the methods adopted for calculating results are as follows: (1) The number of lost-time accidents (numerical strengths of competing units in this case must, of course, be approximately equal); (2) number of lost-time accidents per cent. of employees; (3) the severity rate of accidents; (4) the frequency rate; (5) combined frequency and severity rates; (6) the largest number of man-days or man-hours completed free from lost-time accidents; (7) each unit competing against its own former record.

One of the most important features of the competitions is that they place a new value on accident figures and provide additional uses for them. Instead of these statistics being merely records for the private information of a few persons in the company, competitions make it essential that regular statistical information is supplied to those responsible for the competing units, to foremen and safety committees, etc. Such information stimulates the units to determine the causes of their positions in the competition, and if they are low on the list to concentrate on the deficiencies which have let them down. For example, it might be found that an undue number of accidents has been caused through handling sheet metal, an investigation reveals that the gloves used are not satisfactory, a better type is supplied, and the number of accidents reduced. It is essential that the men be kept continually aware of the progress of the contest. Graphic schemes of showing results usually attract much attention; these can be represented by an aeroplane race, accident thermometer, horse-race, etc.

It is also desirable to introduce propaganda which is incidental to, but running concurrently with, the competition. At one of our works the manager erected a long ladder at the side of one of the silos, and on it placed the figure of a man made in sheet metal. The "tin-man," as he was called, was raised one rung each day there was no lost-time accident. Directly an accident happened the man was brought to the foot of the ladder and had to start all over again. Safety has developed to such a high level at this works that it has now been found necessary to make the rungs of the ladder record weeks instead of days.

Another idea which has found favour in our works is the "No Accident" flag scheme. A flag-staff is erected in a prominent position on the works, and immediately a full week is completed without a lost-time accident a flag, worded "No Accidents," is hoisted. Immediately a lost-time accident occurs the flag is lowered, and it is not put up again until a full week is completed without a lost-time accident. When works improve their records to such an extent that the flag is rarely ever taken down, the introduction of a board showing man-hours worked since the last lost-time accident can be substituted.

For these types of competition it is usual to provide a challenge trophy for the winning unit, and in addition something which will act as a permanent record of the achievement and has not to be passed on to another unit. We have a silver

figure which represents a knight fully armed and on guard—a symbol that men must be adequately protected and always on guard. A concrete and bronze plaque is also provided for the winning unit, and both awards are presented at a function specially held for the purpose. The presentation of these awards should always be made a big event. Money prizes for individuals in the winning unit are not generally looked upon with favour in this country, it being argued that it is just as foolish to reward a man for being safe as it is to pay him for being honest. Prizes in kind are sometimes given without creating the suspicion that the man is being bribed to look after his own safety. A novel form of prize presented by an employer to each of the men in a small winning unit was a pair of safety boots.

We have had an inter-works competition, covering from 21 to 25 factories, in existence during the past eleven years. During that period the combined frequency rate has been gradually lowered from 5.10 to 2.91. We realise, however, that there is still room for improvement, but having regard to the fact that reconstruction work is frequently in progress, and the maintenance of the heavy plant used in the industry is high, we are satisfied that the competition has made a very big contribution to the results.

Competitions soliciting entries from individuals make many employees give thought to safety. Prizes can be awarded for the best original slogan, the best wording for a poster design, or the best suggestion for making any part of the factory or works plant safer. Entry forms should be issued to every individual in the works; no doubt many will be wasted, but a number will get into the homes of employees and will promote discussion and thought on the subject.

At certain periods of the year interest and enthusiasm begin to flag, and in order to effect a revival an intensive campaign is necessary. These campaigns can be for a period of a week or a month at the time of the year when the number of accidents is usually highest. Apart from competitions for individuals, special meetings might be held either during or out of working hours. If they are held during working hours the fact that the employers are prepared to hold such meetings in works' time conveys to the men the seriousness the company attaches to accident prevention. We recently held meetings of all employees in the company's time at fifteen of our factories, and are satisfied that they were of considerable value.

Special efforts may be designed to combat a particular hazard that is causing concern—for example, it might be found that odd rivets lying about are a constant cause of accidents. Concentrated efforts are therefore instituted to collect, on a specified day, as many of these as possible—the quantities collected may be a revelation! Similarly it might be possible to hold a "Nail Day" or an "Unsafe Ladder Day." The results should be made known to the men. Visits of parties of foremen and other responsible persons to the Home Office Museum are undoubtedly well worth while. A display lorry owned by the Association or the Home Office might be of value if it were stationed for a day or two in a prominent position in the works.

Standard Solutions for the Cement Chemist.

NORMAL SULPHURIC ACID (= 49 grammes H_2SO_4 per 1,000 c.c.).—Measure 60 c.c. of pure concentrated sulphuric acid (density = 1.84) and slowly add to 1,000 c.c. of distilled water in a large flask. When cold transfer to a Winchester bottle and dilute to 2,000 c.c.

STANDARDISATION BY GRAVIMETRIC ESTIMATION AS BaSO_4 .—Into each of two 250-c.c. beakers run 10 c.c. of the above acid from a burette. Add 60 c.c. of distilled water and 3 of drops concentrated HCl to each. Place 80 c.c. of 5 per cent. barium chloride solution in a third beaker. Bring the contents of all three beakers to the boil at the same time. To each of the boiling acid liquors slowly add 35 c.c. of boiling barium chloride solution while stirring. Boil for 20 minutes, allow to cool, and stand for three hours. Filter on Swedish ashless filter papers and wash with hot distilled water until the washings are free from chlorides. Dry the precipitates and ignite in platinum.

Example: Weight of BaSO_4 . Determination 1 = 1.1742 gr.

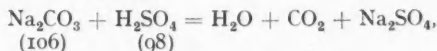
" " " " 2 = 1.1788 gr.

Average = 1.1765 gr.

This corresponds to $1.1765 \times 0.42 = 0.49413$ gr. H_2SO_4 . Thus 1,000 c.c. of sulphuric acid solution contains 49.413 gr. of H_2SO_4 . An alternative method of standardisation, which lacks the gravimetric precision of the above, is by means of sodium carbonate.

NORMAL SODIUM CARBONATE (53 gr. Na_2CO_3 per litre).—Weigh out exactly 5.3 gr. of pure dry Na_2CO_3 (prepared by igniting pure sodium bicarbonate to constant weight at a temperature not exceeding 300 deg. C.). Dissolve in distilled water and make up to 100 c.c.

STANDARDISATION OF SULPHURIC ACID BY SODIUM CARBONATE.—Take 20 c.c. of normal Na_2CO_3 solution in a conical flask; dilute with 25 c.c. of distilled water, add 2 drops of methyl orange, and titrate with the sulphuric acid from a burette. Supposing 19.85 c.c. of H_2SO_4 solution are required for neutralisation of 20 c.c. of normal Na_2CO_3 solution we have



or 20 c.c. of normal Na_2CO_3 solution = 0.98 gr. H_2SO_4 .

Then 19.85 c.c. H_2SO_4 solution contain 0.98 gr. H_2SO_4 , or 1,000 c.c. H_2SO_4 solution contain 49.370 gr. H_2SO_4 .

DILUTION OF SULPHURIC ACID TO TRUE NORMAL.—1,000 c.c. of true normal sulphuric acid contain 49 gr. of H_2SO_4 ; 1,000 c.c. of the solution made up contain 49.413 gr. H_2SO_4 ; 49.413 gr. of H_2SO_4 are contained in $\frac{49.413 \times 1,000}{49}$
= 1,008.4 c.c. of true normal acid. Thus each 1,000 c.c. of solution made up requires mixing with 8.4 c.c. of distilled water to produce true normal solution.

NORMAL SODIUM HYDROXIDE SOLUTION (40 gr. NaOH per litre).—This solution should be prepared free from carbon dioxide by the following method. Take 88 gr. of "pure" sodium hydroxide and dissolve in about 1,500 c.c. of distilled water in a 2-litre flask. Add 15 gr. of freshly slaked lime made into a milky paste with water. Boil for 15 minutes and, when cool enough, pour into a Winchester bottle. Make up to 2,000 c.c., stopper, and allow to settle overnight. Next morning syphon off the clear liquor into a Winchester bottle. Standardise against normal sulphuric acid, using phenolphthalein indicator.

NORMAL POTASSIUM HYDROXIDE SOLUTION (56 gr. KOH per litre).—Prepare as in making standard sodium hydroxide, but use 114 gr. of potassium hydroxide. Standardise against normal sulphuric acid using phenolphthalein indicator.

NORMAL HYDROCHLORIC ACID SOLUTION (36.45 gr. HCl per litre).—Dilute 300 c.c. of pure concentrated hydrochloric acid solution (specific gravity 1.16) to 2,000 c.c. Standardise against normal sodium hydroxide using phenolphthalein indicator.

STANDARD POTASSIUM BICHROMATE (for estimation of Fe in cement).—Weigh 3.074 gr. of dry "analar" potassium dichromate and dissolve in 250 to 300 c.c. of cold water. Pour the solution into a graduated litre flask. Rinse out the beaker several times into the flask and dilute the solution to the litre mark; 1 c.c. of this solution should be equivalent to 0.005 gr. of ferric oxide (Fe_2O_3).

To standardise the solution, weigh into a 250-c.c. beaker 0.4900 gr. of "analar" ferrous ammonium sulphate $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; equivalent to 0.1 gr. of ferric oxide. Dissolve in 50 c.c. of water and, when all the salt is in solution, add 5 c.c. of dilute hydrochloric acid. Now add 20 c.c. of concentrated phosphoric acid and 3 drops of a 1 per cent. solution of diphenylamine in concentrated H_2SO_4 . Dilute to 150 c.c. and titrate with the bichromate. The end point is taken when one drop causes the production of an intense violet-blue colour which is permanent; 20 c.c. of bichromate should be required. Repeat the test. If the first and second results agree divide 0.1 (the Fe_2O_3 equivalent of the ferrous ammonium sulphate used) by the number of cubic centimetres of bichromate required. The result will give the ferric oxide equivalent in grammes for each cubic centimetre of the standard bichromate.

STANDARD POTASSIUM PERMANGANATE (for CaO estimation).—11.5 gr. of "analar" potassium permanganate are weighed out and transferred into a Winchester bottle. Now add two litres of water. Keep in a dark place for 24 hours with frequent shaking. Filter through glass wool into another Winchester bottle which has been painted with black enamel to exclude light. Allow to stand for a week. The solution is now standardised against a cement with a known lime content determined gravimetrically.

Weigh 0.5 gr. of the cement into a 600-c.c. beaker and add, with constant stirring, 10 to 15 c.c. of cold water. Stir and gradually add 15 c.c. of concentrated HCl. Dilute with water and heat a little. The cement should then be completely dissolved without separation of silica. Warm the solution and carefully add dilute ammonia to the solution until a very slight permanent precipitate

forms. Now add 10 c.c. of 10 per cent. oxalic acid solution, when the slight precipitate of R_2O_3 dissolves, leaving a very slight precipitate of calcium oxalate. Add 200 c.c. of boiling water and bring the whole to the boil. Now add gradually, with stirring, 50 c.c. of hot saturated ammonium oxalate solution to precipitate the lime. Simmer and stir for about 10 minutes. Remove from the heat and allow the precipitate to settle. Filter, wash three times by decantation and ten times on the filter, using not more than 10 to 15 c.c. of water each time. Remove the filter from the funnel, open it, and lay it against the side of the beaker in which the precipitation was made. Wash from the paper into the beaker with hot water, add 25 c.c. of dilute sulphuric acid and 100 c.c. of hot water. Stir and heat to 80 to 90 deg. C. until all precipitate is dissolved. Titrate at 80 to 90 deg. C. with permanganate until a faint pink colour persists. Now drop in the filter paper, stir until the colour is discharged, and finish the titration carefully drop by drop.

Indicators.

ALCOHOLIC PHENOLPHTHALEIN.—Dissolve 1 gr. of phenolphthalein in 100 c.c. of 50 per cent. alcohol. Phenolphthalein is a very delicate indicator and is very susceptible to carbon dioxide; solutions to be titrated must be freed from the latter by boiling whenever this indicator is used. It is also useless in the presence of free ammonia or its compounds.

METHYL ORANGE.—Dissolve 0.1 gr. of methyl orange in 100 c.c. of distilled water. Whilst not so delicate as phenolphthalein the advantages of methyl orange are that it can be used in the cold with carbonates, and its delicacy is not impaired by the presence of ammonia or its salts.

LITMUS SOLUTION.—Digest the solid with distilled water for several hours; decant or filter; render neutral by acetic acid or ammonia. Store in a bottle with access of air.

Bench Reagents.

("AR" = analytical, or "analar," reagents.)

Acetic acid	Glacial (AR).
Acetic acid (5N)	Dilute 735 cc. glacial (AR) acetic acid to 2,500 c.c.
Alcohol	Absolute.
Ammonium carbonate (5N)	(AR). 492 gr. dissolved in 2N. NH_4OH (2,083 c.c.) and diluted to 2,500 c.c.
Ammonium chloride (2N)	(AR). 268 gr. in hot water. Dilute to 2,500 c.c.
Ammonium hydroxide	(AR). Sp. gr. 0.88. Test with $CaCl_2$ to see that it is free from ammonium carbonate.
Ammonium hydroxide (10%)	275 c.c. 0.88 ammonia diluted to 2,500 c.c.
Ammonium molybdate	250 gr. (AR) dissolved in hot water. Allow to stand, filter, and dilute to 2,500 c.c.
Ammonium nitrate	1 gr. (AR) per 100 c.c. water.
Ammonium oxalate	Saturated. 106 gr. dissolved in 2,500 c.c. of water.

Barium chloride	Dissolve 250 gr. in warm water and dilute to 2,500 c.c.
Bromine water	Make a saturated solution using (AR) bromine saturated solution = 3.66 per cent. bromine by weight.
Calcium carbonate	(AR).
Cleaning acid	Commercial chromic acid in strong sulphuric acid.
Calcium chloride	Normal solution. 139 gr. (AR) CaCl_2 in 2,500 c.c. of water.
Calcium hydroxide	Saturated solution contains about 0.17 per cent. by weight of Ca(OH)_2 .
Hydrogen peroxide	20 volumes (AR).
Hydrochloric acid	(AR). Concentrated.
Hydrochloric acid (5N)	880 c.c. of concentrated acid plus 1,120 c.c. of water.
Hydrofluoric acid	(AR).
Mercuric chloride	130 gr. (AR) to 2,500 c.c. of water.
Nitric acid	(AR). Concentrated.
Nitric acid (5N)	644 c.c. of concentrated acid plus 1,357 c.c. of water.
Oxalic acid	238 gr. dissolved and made up to 2,500 c.c.
Phosphoric acid	(AR). Concentrated.
Perchloric acid	(AR). 65 per cent.
Potassium perchlorate	(AR).
Potassium hydroxide	(AR). Pellets.
Potassium chromate	(AR). 5 per cent. solution made neutral and free from chloride.
Potassium nitrate	(AR).
Sodium carbonate	175 gr. (AR) sodium carbonate dissolved and diluted to 2,500 c.c.
Sodium acetate	(AR).
Sodium pyrosulphate	(AR). Fused.
Sodium hydroxide	(AR).
Sulphuric acid	(AR). Concentrated.
Sulphuric acid (5N)	292 c.c. of concentrated acid plus 1,940 c.c. of water.
Stannous chloride	100 gr. of stannous chloride (AR) in a mixture of 300 c.c. of water and 100 c.c. of hydrochloric acid (AR, concentrated). Boil until the solution is clear and colourless. Keep the solution in a closely stoppered bottle containing metallic tin.

The Thermal Efficiency of the Rotary Cement Kiln.*

By HANS GYGI (Zurich.)

(Continued.)

IV.—HEAT TRANSFER.

(2) CALCULATION OF THE QUANTITY OF HEAT TRANSFERRED TO THE MATERIAL FOR 1 M. OF KILN LENGTH.—Although it is of primary interest to know in what manner the gases give up their heat during their passage through the kiln, knowledge of the way in which heat is transferred to the material is also desirable. To commence with, we can state that heat is transferred to the material by radiation from the gases and from the wall, by convection from the gases and by conduction from the wall or lining. This quantity of heat corresponds to the difference between the heat given up by the gases and the radiation losses from the outer surface of the kiln casing. The process can therefore be expressed

$$Q_{\text{Gas}} - Q_{\text{Radiation kiln casing}} = Q_{\text{Radiation G.M.}} + Q_{\text{Radiation W.M.}} + Q_{\text{Convection G.M.}} + Q_{\text{Conduction W.M.}} \quad (23)$$

The heat radiated from the wall to the material can be calculated from the law of Stephan and Boltzmann, but it must be borne in mind that the gases, which contain carbon dioxide and water vapour, will absorb a part of this radiation. The best way of taking this into account is to introduce a "permeation coefficient" as was done by W. J. Wohlenberg^{22, 23} and his colleagues in their investigation of the radiation from the flame in the combustion chambers of steam boilers fired with pulverised coal.

According to Wohlenberg the "permeation coefficient" depends upon the temperature of the radiating body and is defined by

$$L = \frac{q_{\text{black}} - (q_{\text{CO}_2} + q_{\text{H}_2\text{O}})}{q_{\text{black}}}$$

into which for L_w , the temperature of the wall, and for L_m , the temperature of the material, are to be introduced.

The equation for the heat transfer by radiation from the lining to the material can then be written

$$Q_{\text{Radiation W.M.}} = F_m C \left[L_w \left(\frac{T_w}{100} \right)^4 - L_m \left(\frac{T_m}{100} \right)^4 \right] \quad (25)$$

In order that equation (25) shall be valid we shall assume that the mean temperatures of the walls and the material in the adjacent zones differ so little from those at the cross section under consideration that their effect on radiation is negligible.

We must now consider what value is to be assigned to C in equation (25). As it is not possible to calculate this value simply and reliably for the case in point, we are obliged to determine C by analogy with the radiation properties of

* Continued from "Cement and Lime Manufacture," November and December, 1937, and February, March and April 1938.

the hollow body. The surface formed by the material is enveloped by the wall of the kiln which radiates heat and may therefore be likened to an imperfect hollow body irradiating the material to be burned through an opening corresponding to the surface formed by the material in the kiln. We can therefore determine the radiation emitted by the hollow body by assuming that a surface equivalent in area to the opening in the hypothetical hollow body radiates heat at a temperature equal to the mean temperature of the exposed kiln lining and with a radiation coefficient a little greater than that of the material of which the lining is composed. Furthermore, equation (25) can only be regarded as an approximation, because it takes no account of the fact that part of the radiation from the wall to the material is reflected.

We shall now consider what method can be used to calculate the heat transfer from the lining to the material by conduction from the temperature distribution over the inner surface of the lining during one revolution of the kiln.

The unidimensional heat flow in a solid body in the direction of the x -axis of a system of co-ordinates is given by Fourier's differential equation

$$\frac{\partial \theta}{\partial t} = a \frac{\partial^2 \theta}{\partial x^2} \quad \dots \quad (26)$$

in which

θ = temperature,

x = abscissa,

t = time,

$a = \frac{\lambda}{c \times \gamma}$,

λ = thermal conductivity,

c = specific heat, and

γ = specific gravity.

By assuming a periodic temperature distribution, we obtain a solution of equation (26) in the form

$$\theta = \sum_{v=1}^{\infty} A_v e^{-\mu_v x} \cos(v\omega t - \mu_v x - \alpha_v) \quad \dots \quad (27)$$

which represents the penetration of a periodically fluctuating surface temperature into the interior of a solid bounded by a plane and in which x is the distance from the surface.

Further

v = a whole number,

$\mu_v = \sqrt{\frac{\omega v}{2a}}$,

$\omega = \frac{2\pi}{t_0}$,

t_0 = the period,

$a = \frac{\lambda}{c\gamma}$, and

A_v and α_v = constants to be determined from the boundary conditions.

The temperature θ_0 at the surface of the solid, that is to say where $x = 0$, is

$$\theta_0 = \sum_{v=1}^{\infty} A_v \cos(v\omega t - \alpha_v) \quad \dots \quad (28)$$

and the heat flow at the point x at the time t is

$$q = -\lambda \frac{\partial \theta}{\partial x} \quad \dots \quad (29)$$

when the heat flow in the direction of the positive x -axis is taken to be positive.

From equation (27)

$$q = \lambda \sum_{v=1}^{\infty} A_v e^{-\mu_v x} \mu_v [\cos(v\omega t - \mu_v x - \alpha_v) + \sin(v\omega t - \mu_v x - \alpha_v)] \quad \dots \quad (30)$$

At the surface, when $x = 0$,

$$q_0 = -\lambda \sum_{v=1}^{\infty} A_v \mu_v [-\cos(v\omega t - \alpha_v) + \sin(v\omega t - \alpha_v)]$$

or

$$q_0 = \lambda \sum_{v=1}^{\infty} A_v \mu_v \sqrt{2} \cos\left[v\omega t - \left(\alpha_v - \frac{\pi}{4}\right)\right] \quad \dots \quad (31)$$

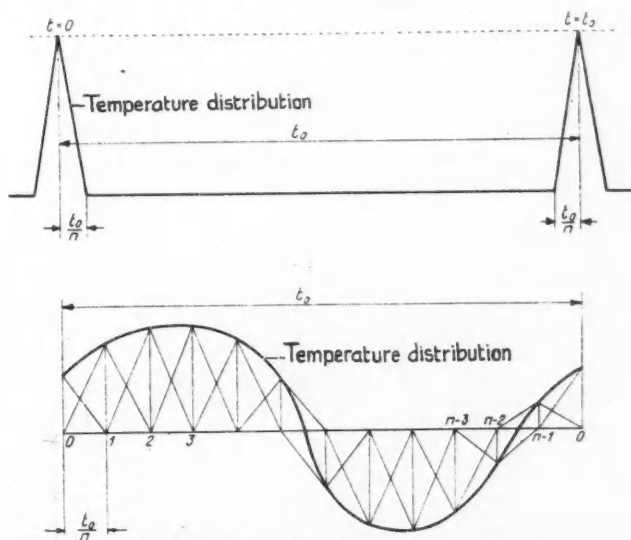


Fig. 22.—Triangular form of temperature curve for the surface of the lining and the general periodic temperature curve obtained from a succession of peaks.

To calculate q_0 , it is advantageous to use the method given by Professor Kirsch²⁴. We shall therefore first determine the form of the heat flow at the surface for a triangular temperature distribution as shown in Fig. 22, in which the height of the apex is equal to the unit of temperature and half the base of the triangle is $\frac{1}{n} t_0$, n being a whole number. It must be possible to represent this temperature

distribution by the Fourier series in equation (28). The analysis for the triangular temperature distribution gives

$$\alpha_1 = \alpha_2 = \dots = \alpha_v = 0$$

$$A_v = \frac{n}{\pi^2 v^2} \left[1 - \cos \left(\frac{2\pi}{n} v \right) \right] \quad \dots \quad (32)$$

There is a constant term in this Fourier series corresponding to the mean value of the temperature over the period and the differential equation (26) is still satisfied if it is introduced. But in the derivation from x it disappears and therefore need not be taken into account in the calculation of the heat flow.

Substituting A_v and $\alpha_v = 0$ in equation (31) and bearing in mind that

$$\mu_v = \sqrt{\frac{v\omega}{2a}} = \sqrt{\frac{v\omega c\gamma}{2\lambda}}$$

we have

$$q_0 = \sqrt{\omega\lambda c\gamma} \sum_{v=1}^{\infty} \frac{n}{\pi^2 v^{3/2}} \left[1 - \cos \left(\frac{2\pi}{n} v \right) \right] \cos \left(v\omega t + \frac{\pi}{4} \right) \quad \dots \quad (33)$$

or, if we write

$$B_v = \frac{n}{\pi^2 v^{3/2}} \left[1 - \cos \left(\frac{2\pi}{n} v \right) \right],$$

$$q_0 = \sqrt{\omega\lambda c\gamma} \sum_{v=1}^{\infty} B_v \cos \left(v\omega t + \frac{\pi}{4} \right) \quad \dots \quad (34)$$

Now, if we take a finite number of terms for the Fourier series we shall not obtain an exact representation of the triangular temperature distribution, but the more terms we take the nearer shall we approximate to the temperature distribution and therefore to the heat flow. The first 24 coefficients A_v and B_v are given in Table 13 for $n = 12$, that is, when the half base of the triangle is $\frac{1}{12} t_0$.

TABLE 13.—COEFFICIENTS A_v AND B_v FOR THE FIRST 24 TERMS OF THE FOURIER SERIES.

v -Values	A_v -Values	B_v -values	v -Values	A_v -Values	B_v -values
1	0.16290	0.16290	13	0.00096	0.00348
2	0.15198	0.21494	14	0.00310	0.01161
3	0.13509	0.23372	15	0.00540	0.02093
4	0.11399	0.22797	16	0.00712	0.02850
5	0.09075	0.20293	17	0.00785	0.03237
6	0.06755	0.16546	18	0.00751	0.03184
7	0.04630	0.12250	19	0.00629	0.02740
8	0.02850	0.08060	20	0.00456	0.02039
9	0.01501	0.04503	21	0.00276	0.01263
10	0.00608	0.01922	22	0.00126	0.00589
11	0.00135	0.00447	23	0.00031	0.00148
12	0.00000	0.00000	24	0.00000	0.00000

If we write

$$\sum_{v=1}^{24} B_v \cos \left(v\omega t + \frac{\pi}{4} \right) = y(t) \quad \dots \quad (35)$$

then, approximately,

$$q_0 = \sqrt{\omega \lambda c \gamma} \cdot y$$

For various values of t , at intervals of $\frac{t_0}{12}$, y has the values given in Table 14.

TABLE 14.— y AS A FUNCTION OF $\frac{t_0}{12}$.

Stages	t -Values	y -Values	Stages	t -Values	y -Values.
0	0	+1.18541	7	$7 \frac{t_0}{12}$	-0.03881
1	$1 \frac{t_0}{12}$	-0.75217	8	$8 \frac{t_0}{12}$	-0.03417
2	$2 \frac{t_0}{12}$	-0.17373	9	$9 \frac{t_0}{12}$	-0.03290
3	$3 \frac{t_0}{12}$	-0.09917	10	$10 \frac{t_0}{12}$	-0.02557
4	$4 \frac{t_0}{12}$	-0.06981	11	$11 \frac{t_0}{12}$	+0.13757
5	$5 \frac{t_0}{12}$	-0.05435	12=0	0	+1.18541
6	$6 \frac{t_0}{12}$	-0.04491			

If the height of the temperature peak, when $x = 0$ and $t = 0$, is not unity but θ_{00} , then

$$q_0 = \sqrt{\omega \lambda c \gamma} \cdot \theta_{00} y \quad \dots \quad (36)$$

The heat flow at the i -th stage, where $t = i \frac{t_0}{12}$, is

$$q_{0i} = \sqrt{\omega \lambda c \gamma} \cdot \theta_{00} y_i \quad \dots \quad (37)$$

The graphical representation of a general periodic temperature distribution by the superimposition of the peaks of a triangular temperature distribution makes it possible to calculate the heat flow by super-imposition (see Fig. 22).

The k -th peak gives a distribution of heat flow according to equations (36) and (37) in which, however, θ_{0k} is to be substituted for θ_{00} . Furthermore, the heat-flow distribution so obtained must be displaced by k stages. We thus have

$$q_{0i} = \sqrt{\omega \cdot \lambda \cdot c \cdot \gamma} \cdot \theta_{0k} \cdot y_{i-k} \quad \dots \quad (38)$$

for the heat flow at the i -th stage in consequence of the k -th temperature peak.

The superimposition of all the peaks gives

$$q_{0i} = \sqrt{\omega \cdot \lambda \cdot c \cdot \gamma} \cdot \sum_{k=0}^{k=11} \theta_{0k} \cdot y_{i-k} \quad \dots \quad (39)$$

for the heat flow at the i -th stage.

We can now prepare a chart (Table 15) in which the temperatures θ_{00} , θ_{01} , θ_{02} , θ_{03} , . . . θ_{012} are known from the readings taken during one revolution of the kiln, and the coefficients y_1 , y_2 , y_3 , y_4 , . . . y_{12} can be taken from Table 14.

For any period, the mean heat flow found is always zero; but the stationary heat flow, in the rotary kiln, $q_{\text{Radiation kiln casing}}$ must be added to this.

In view of the thermal stresses set up by the temperature fluctuations at the surface of the lining, it is of interest to determine the depth to which the periodic

temperature changes penetrate into the kiln lining. The temperature fluctuations at a depth x can be calculated by equation (27)

$$\theta = \sum_{v=1}^{\infty} A_v e^{-\mu_v x} \cos(v\omega t - \mu_v x - \alpha_v) \quad \dots \quad (27)$$

Each term of the summation represents a decreasing fluctuation as a function of x , wherein μ_v is the "damping exponent" and A_v the initial amplitude. As μ_v is proportional to \sqrt{v} , fluctuations of a higher order are more strongly damped than those of a lower order. When the depth x is considerable, only fluctuations of the first order persist and we can restrict ourselves to calculating these.

The amplitude of the fluctuation of the first order is

$$a_1 = A_1 e^{-\mu_1 x} \quad \dots \quad (40)$$

in which A_1 = the amplitude at the surface, and $x = 0$.

TABLE 15.—CHART FOR THE CALCULATION OF THE HEAT FLOW IN THE i STAGES.

$i =$	0	1	2		9	10	11
$k=0$	$n_{00}^k y_0$	$n_{00}^k y_1$	$n_{00}^k y_2$		$n_{00}^k y_9$	$n_{00}^k y_{10}$	$n_{00}^k y_{11}$
$k=1$	$n_{01}^k y_0$	$n_{01}^k y_1$	$n_{01}^k y_2$		$n_{01}^k y_9$	$n_{01}^k y_{10}$	$n_{01}^k y_{11}$
$k=2$	$n_{02}^k y_0$	$n_{02}^k y_1$	$n_{02}^k y_2$		$n_{02}^k y_9$	$n_{02}^k y_{10}$	$n_{02}^k y_{11}$
$k=10$	$n_{010}^k y_0$	$n_{010}^k y_1$	$n_{010}^k y_2$		$n_{010}^k y_9$	$n_{010}^k y_{10}$	$n_{010}^k y_{11}$
$k=11$	$n_{011}^k y_0$	$n_{011}^k y_1$	$n_{011}^k y_2$		$n_{011}^k y_9$	$n_{011}^k y_{10}$	$n_{011}^k y_{11}$
Sum of each col.	C_0	C_1	C_2		C_9	C_{10}	C_{11}
q_0	$\frac{q_{00}^*}{C_0 \sqrt{\omega \lambda c_f}}$	$\frac{q_{01}^*}{C_1 \sqrt{\omega \lambda c_f}}$	$\frac{q_{02}^*}{C_2 \sqrt{\omega \lambda c_f}}$		$\frac{q_{09}^*}{C_9 \sqrt{\omega \lambda c_f}}$	$\frac{q_{010}^*}{C_{10} \sqrt{\omega \lambda c_f}}$	$\frac{q_{011}^*}{C_{11} \sqrt{\omega \lambda c_f}}$

By putting $a_1 = 0.1A$, we can, for example, determine from equation (27) the depth at which the amplitude of the fluctuation is only one-tenth of the initial value.

$$\text{For the value } \mu_1 = \sqrt{\frac{\omega}{2a}} = 289$$

$$x = 7.96 \text{ mm.}$$

Having explained in principle the method by which it is possible to calculate the quantity of heat that is transferred to the material in 1 m. length of the kiln, we now proceed to the numerical expression of equation (23).

$Q_{\text{Radiation G.M.}}$ —The radiation from the gases to the material has already been calculated as

$$Q_{\text{Radiation G.M.}} = 98,300 \text{ Kcal./m.h.}$$

$Q_{\text{Radiation W.M.}}$ —The expression for the radiation from the wall to the material is

$$Q_{\text{Radiation W.M.}} = F_m \cdot C \left[h_w \left(\frac{T_w}{100} \right)^4 - h_m \left(\frac{T_m}{100} \right)^4 \right]$$

Now $h_w = 0.679$ and $h_m = 0.656$, and we can assign the value 4.70 to the radiation coefficient e .

$\therefore Q_{\text{Radiation W.M.}} = 44,000 \text{ Kcal./m.h.}$

$Q_{\text{Convection G.M.}}$ —The heat transferred from the gases to the material by convection has already been calculated as

$Q_{\text{Convection G.M.}} = 10,300 \text{ Kcal./m.h.}$

$Q_{\text{Conduction W.M.}}$ —The heat-flow distribution has been calculated from the temperature distribution at the surface of the lining during one revolution

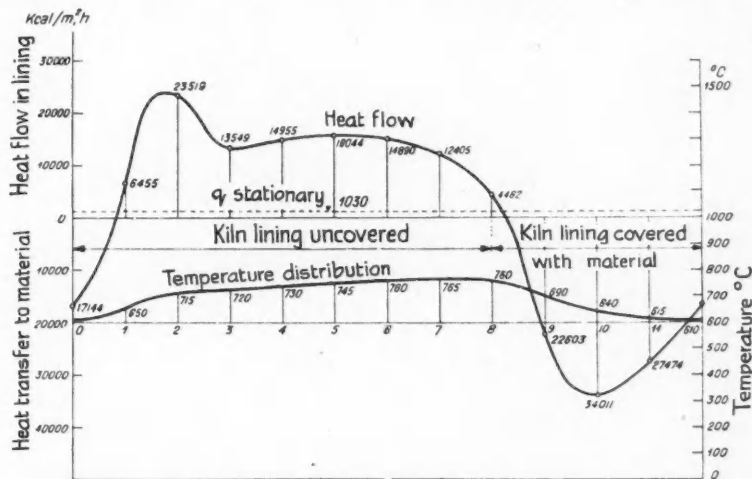


Fig 23.—Temperature distribution and heat flow from the surface of the kiln lining into the wall of the kiln, and transfer of heat from kiln wall to material at cross-section 6.

of the kiln by Kirsch's method previously described. This gave for the heat flow at the i -th stage, for the approximate temperature distribution assumed,

$$q_{0i} = C_1 \sqrt{\omega \cdot \lambda \cdot c \cdot \gamma}$$

in which

$$\omega = \frac{2\pi}{t_0} = \frac{2\pi \cdot 3600}{78} = 289.84 \text{ h}^{-1}$$

$$\lambda = 0.8 \text{ Kcal./m.h. deg. C.}$$

$$c = 0.256 \text{ Kcal./kg.}$$

$$\gamma = 1,800 \text{ kg./m}^3$$

so that

$$\sqrt{\omega \lambda c \gamma} = 326.88.$$

In Table 16 the values for C and q are given for the twelve stages. If we now take into account the stationary heat flow, which is 1,030 Kcal./m²h., we have all the data necessary to plot the curves shown in Fig. 23. This figure shows a projection of the circumference of the kiln on which the temperature distribution and the heat flow per unit of time and unit of area are plotted. The figure also shows the part of the kiln lining from which heat flows into the material, so that

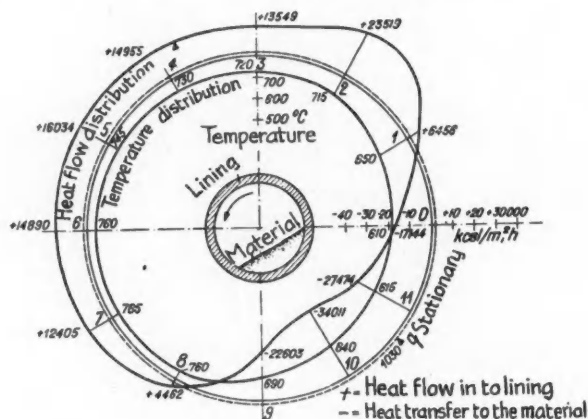


Fig. 24.—Temperature, etc., as Fig. 23 shown in cross-section.

the mean heat flow from lining to material by conduction can be determined with a planimeter.

The mean heat flow found in this manner is $q_{\text{conduction}} = 24,850 \text{ Kcal./m.}^2\text{h.}$ If this value be multiplied by the area of the surface of the lining for 1m. length of kiln from which heat flows into the material, the product represents the quantity

Heat Balance at Cross-Section No.6

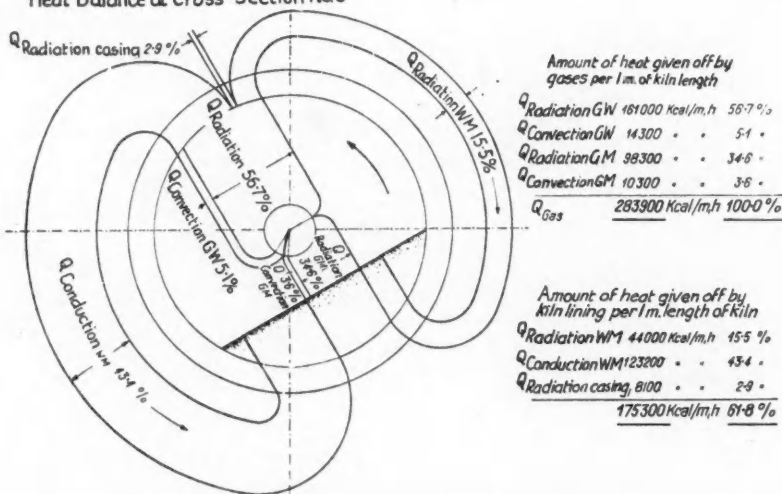


Fig. 25.—Heat balance at cross-section No. 6.

TABLE 16.—VALUES OF C AND q FOR THE i STAGES AT CROSS SECTION 6.

Stages	C_i	q_i Kcal/m ² h	$q_i + q_{\text{stationary}}$ Kcal/m ² h	Stages	C_i	q_i Kcal/m ² h	$q_i + q_{\text{stationary}}$ Kcal/m ² h
0	-55.6	-18,174	-17,144	6	+42.4	+13,860	+14,890
1	+16.6	+5,426	+6,456	7	+34.8	+11,375	+12,405
2	+68.8	+22,489	+23,519	8	+10.5	+3,432	+4,462
3	+38.3	+12,519	+13,549	9	-72.3	-23,633	-22,603
4	+42.6	+13,925	+14,955	10	-107.2	-35,041	-34,011
5	+45.9	+15,004	+16,034	11	-87.2	-28,504	-27,474

of heat which would be transferred to the material from the lining by conduction if the surface of the lining were perfectly plane. To obtain the area of the actual uneven surface of the kiln lining, the area of the hypothetical plane surface must be multiplied by an "unevenness factor" β . Proceeding from the consideration that the lining takes up the same amount of heat from the gases as it gives up to the material and losses through the kiln casing, the value for the "unevenness factor" is found to be about 2.4. We now have

$$Q_{\text{Conduction W.M.}} = q_{\text{Conduction W.M.}} \cdot F_l \cdot \beta$$

$$Q_{\text{Conduction W.M.}} = 123,200 \text{ Kcal./m.h.}$$

Fig. 24 shows heat flow and temperature distribution during a revolution of the kiln in a somewhat different form, which may give a clearer idea of the process.

We are now able to give the heat transfer to the material for 1 m. length of kiln :

$$\begin{aligned} Q_{\text{Radiation G.M.}} &= 98,300 \\ Q_{\text{Radiation W.M.}} &= 44,000 \\ Q_{\text{Convection G.M.}} &= 10,300 \\ Q_{\text{Conduction W.M.}} &= 123,200 \end{aligned} \text{ Kcal./m.h.}$$

$$Q_{\text{Gas}} - Q_{\text{Radiation kiln casing}} = 275,800 \text{ Kcal./m.h. (calculated).}$$

On the other hand, we have from our experimental results

$$\begin{aligned} Q_{\text{Gas experimental}} &= 286,000 \\ Q_{\text{Radiation kiln casing experimental}} &= 8,100 \end{aligned} \text{ Kcal./m.h.}$$

$$Q_{\text{Gas}} - Q_{\text{Radiation kiln casing experimental}} = 277,900 \text{ Kcal./m.h.}$$

so that there is very good agreement between the measured and the calculated values.

The heat transfer from the gases, the heat transfer to the material, and the radiation losses from the kiln casing as determined by the previous method of calculation are shown graphically in Fig. 25.

(To be continued.)

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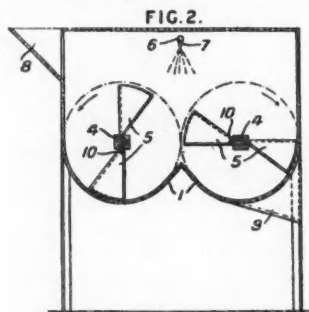
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Recent Patents Relating to Cement.

Cement Manufacture.

474,574. Krupp Akt.-Ges., April 5, 1937.

The process described in the parent specification for loosening finely-powdered material, such as raw cement meal, prior to sintering is modified by throwing up the particles from the mass in the form of a shower, as far as possible without allowing them to touch the walls of the container and in particular without pressing or throwing them against the walls. The loosening treatment may be carried out in containers which operate intermit-



tently, or in apparatus which conveys the material during treatment. In the former case the material may be thrown up towards the central vertical axis of the container by rapidly-whipping wings. In the latter case the treatment may be carried out in an inclined trough and the material may be thrown by means of two wing shafts in an oblique upward direction towards the centre of the trough.

Trade Notice.

Steel Castings.—Messrs. David Brown & Sons (Huddersfield), Ltd., at their Penistone foundries, now make carbon steel and alloy steel castings by a special process which differs essentially from the orthodox method, enabling moulds possessing a high degree of permeability and with a surface entirely resistant to metal to be produced. Due to the greater rigidity and hardness of the moulds, it is claimed that castings much truer to the pattern are obtained with smoother and better surfaces and having excellent machining qualities. It is also claimed that steel possessing the highest degree of homogeneity is assured by the use of high-frequency furnaces having close temperature control. Three furnaces are in operation with capacities of 5, 15 and 40 cwt., annealing or heat treatment of castings being carried out in bogie-hearth electric furnaces. Castings weighing up to 25 cwt. each are now being made by this new process.

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As shown, two oppositely-rotating parallel shafts (4) arranged within a container (1) carry a number of inclined wings (5) fixed by nuts (10) and capable of being angularly adjusted. The material is fed in through an inlet (8) at one end of the container and is whipped up and fed along by the two sets of rotating wings, being finally withdrawn through an opening (9) at the other end. At the top of the container is a water pipe (6) with atomizing nozzles (7).